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NEW LASER DYE SYSTEMS BASED ON TRANSITION METAL COMPLEXES.(U)
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Excited state properties of luminescent ruthenium(II) complexes and their interactions with laser dyes, other metal complexes, and oxygen have been studied in both homogeneous and surfactant containing solutions and in solid polymer matrices. Low cost experimental tools have been developed to facilitate these studies. These include a low cost temperature controller, a simple deoxygenation cell for surfactant solutions, and a low frequency com-

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20. Abstract

puterized lockin amplifier. Also, new quantum counters for light intensity measurements have been developed.

Energy transfer from ruthenium(II) complexes to a variety of rhodamine and oxazine laser dyes has been demonstrated in both homogeneous solutions and in surfactant-assisted ones. Singlet energy transfer efficiencies from the charge transfer (CT) sensitizing state of the Ru(II) complex to the laser dyes in homogeneous solutions are unity, and in surfactant-assisted systems efficiencies are 45-75% at concentrations of 10^{-5}M.

Excited state interactions of cation exchange bound Ru(II) complexes $[Ru(bpy)_3]^{2+}$ have been studied using molecular oxygen as a probe of the binding sites. Singlet oxygen formation efficiencies approach 85% under favorable conditions. These efficiencies exceed those of the common heterogeneous singlet oxygen generators. A model for the system has been developed.

19. Key Words

lasers, metal complexes, Ruthenium(II), dyes, quantum counters, actinometer, energy transfer, excited state, alpha-diimine, luminescence, singlet oxygen, deconvolution, electrontransfer surfactants, boxcar integrator, photon yields, kinetics, microcomputer, intersystem crossing, rhodium(III), risetimes, excited-state acid-base, bolometer, charge transfer luminescence, text editor, ferrioxalate, temperature controller, mercury(II), mercury(I).

AFOSR-TR- 82-0662

FINAL REPORT

NEW LASER DYE SYSTEMS BASED ON TRANSITION METAL COMPLEXES

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AFOSR-78-3590

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JUNE 1, 1978 - MAY 31, 1982

B. Research Objectives.

1. To study excited-state properties of luminescent transition metal complexes and their excited state interactions with laser dyes, metal complexes, and oxygen.

2. To study the mechanism of energy and electron transfer processes between metal complexes and other molecules.

3. To utilize energy transfer between metal complexes and laser dyes in order to develop new and improved binary laser dye systems with enhanced stability, efficiency and narrower line widths.

4. To develop new classes of luminescent metal complexes which can be used in the above studies.

5. To develop novel photochemical and spectroscopic tools to permit or facilitate the above studies.

C. Summary of the Research Effort

Major goals of this study have been the elucidation of the photochemical and photophysical processes of platinum metal complexes. While no new laser dye systems have been developed, the fundamental studies necessary to develop binary laser dye systems have been completed. The work has also led to a further understanding of the excited state processes in Ru(II) photosensitizers and to the development of a variety of new chemical systems. We briefly summarize our results with full details given in the publications listed in Part D.

Contrary to the widely-held view that the charge transfer (CT) excited states of Ru(II) complexes, are triplet states, we have demonstrated experimentally that they possess a great deal of singlet character. This has been shown using diffusional singlet energy transfer to the singlet states of laser dyes. This result also shows that the metal complexes can potentially be used as energy antenna in binary laser dye systems. Very efficient micellar-enhanced singlet energy transfer has also been demonstrated. Models for the binding of Ru(II) photosensitizers to nonionic surfactants were developed. Charge surfactants have been used to impede quenching and electron transfer reactions.

Polymer supported tris(2,2'-bipyridine)ruthenium(II) has also been studied as a heterogeneous singlet oxygen generator. A model of the structure of the binding sites and the routes by which singlet oxygen reactions occur in these systems has

been developed.

There was a widely held view that fully ring aromatized polypyridine ligands were required with platinum metal complexes to yield CT photosensitizers. We have demonstrated that only the α-diimine functionality need be present for CT luminescence. This opens up an entirely new class of CT excited state photosensitizers.

The first example of an excited state acid base reaction of a complex exhibiting CT luminescence was reported. A unique inversion of the lowest state was observed on protonation. On protonation the CT state rose above the lowest π-π^* triplet state, and the emission changed from a CT one to a π-π^* phosphorescence.

A variety of new tools and techniques were developed. These include mathematical and instrumental methods of luminescence lifetime analysis, calibration of chemical actinometers, new luminescence quantum counter systems based on solid polymer matrices and/or metal complexes, and new methods of studying fast reversible excited state electron transfer reactions. Also developed were a low-cost temperature controller, a rapid surfactant deoxygenation system, and useful computer programs.

D. Technical Publications

1. B. A. DeGraff, J. N. Demas, and D. G. Taylor, "Reversible Excited-State Electron-Transfer Reactions of Transition Metal Complexes", Solar Energy Conversion and Storage, Ed. by R. B. King, C. R. Kutal, and R. R. Hautala, The Humana Press, Clifton, N. J., 189 (1979).

2. D. G. Taylor and J. N. Demas, "Light-Intensity Measurements I. Large Area Bolometers with Microwatt Sensitivities and Absolute Calibration of the Rhodamine B Quantum Counter", Anal. Chem. 51, 712 (1979).

3. D. G. Taylor and J. N. Demas, "Light Intensity Measurements II. Luminescent Quantum Counter Comparator and Evaluation of Some Luminescent Quantum Counters", Anal. Chem. 51, 717 (1979).

4. D. G. Taylor and J. N. Demas, "The Step Excitation Method for Studying Reversible Excited-State Electron-Transfer Reactions: Experimental Realization", J. Chem. Phys. 71, 1032 (1979).

5. W. P. Krug and J. N. Demas, "Charge Transfer Luminescence from an α-Diimine Complex of Ruthenium(II)", J. Am. Chem. Soc. 101, 4394 (1979).

6. S. H. Peterson and J. N. Demas, "Excited-State Acid-Base Reactions of Dicyanobis(2,2'-biyridine)ruthenium(II) and Dicyanobis(1,10-phenanthroline)ruthenium(II)", J. Am. Chem. Soc. 101, 6571 (1979).

7. D. G. Taylor and J. N. Demas, "On the Intersystem Crossing Yields of Ruthenium(II) and Osmium(II) Photosensitizers", Inorg. Chem., 18, 3177 (1979).

8. S. H. Peterson, J. N. Demas, T. Kennelly, H. Gafney, and D. P. Novak, "On the Measurement of Luminescence Risetimes. A Case Study of the Risetimes of Rhodium(III) Complexes", J. Phys. Chem. 83, 2991 (1979).

9. D. G. Taylor, "Excited-State Electron-Transfer Processes of Transition Metal Complexes", Ph. D. Thesis, University of Virginia, 1979.

10. T. J. Turley, "Measurements of Excited State Lifetimes", M. S. Thesis, University of Virginia, 1979.

11. D. G. Taylor, T. J. Turley, M. Rodgers, S. H. Peterson, and J. N. Demas, "A Microcomputer Controlled Boxcar Integrator with Subnanosecond Risetime", Rev. Sci. Instrum. 51, 855 (1980).

12. C. S. Nichols, J. N. Demas, T. H. Cromartie, "A Microcomputer Interfaced Spectrophotometer for Kinetic Analysis", Anal. Chem. 52, 205 (1980).

13. J. N. Demas and S. E. Demas, "A Microcomputerized Text Editor for Scientific and Chemical Manuscripts", J. Chem. Ed. 57, 252 (1980).

14. K. Mandal, T. D. L. Pearson, and J. N. Demas, "Singlet Energy Transfer from the Charge Transfer Excited State of Tris (2,2'-bipyridine)ruthenium(II)", J. Chem. Phys. 75, 2507 (1980).

15. F. W. Reed and J. N. Demas, "An Analysis of Errors in the Phase Plane Method of Deconvolution of Luminescence Lifetimes", NATO Advanced Study Institute Series, Time Resolved Spectroscopy, in press.

16. K. Mandal, T. D. L. Pearson, and J. N. Demas, "Luminescent Quantum Counters Based on Organic Dyes in Polymer Matrices", Anal. Chem. 52, 2184 (1980).

17. K. Mandal, T. D. L. Pearson, and J. N. Demas, "New Luminescent Quantum Counter Systems Based on a Transition Metal Complex", Inorg. Chem. 20, 786 (1981).

18. J. N. Demas, W. D. Bowman, E. F. Zalewski, and R. A. Velapoldi, "Determination of the Quantum Yield of the Ferrioxalate Actinometer with Electrically Calibrated Radiometers", J. Phys. Chem. 85, 2766 (1981)

19. J. M. Greer, F. W. Reed, and J. N. Demas. "Evaluation of Errors in the Phase Plane Method for Deconvolution of Luminescence Lifetime Data", Anal. Chem. 53, 710 (1981).

20. K. Mandal and J. N. Demas, "Surfactant Enhanced Singlet Energy Transfer from the Charge Transfer Excited State of Tris(2,2'-bipyridine)ruthenium(II)", Chem. Phys. Lett. 84, 410 (1981).

21. T. D. L. Pearson, M. J. Greer, and J. N. Demas, "A Program for the Preparation of Posters and Overhead Transparencies", J. Chem. Ed. 58, 691 (1981).

22. J. Toney and J. N. Demas, "Low Frequency Computerized Lock-In Amplifier", Rev. Sci. Instrum., 53, 1082, (1982).

23. S. Buell and J. N. Demas, "Low Cost Temperature Controller", Anal. Chem. 54, 1214 (1982).

24. J. N. Demas, "The Measurement of Photon Yields", in Photoluminescence Spectrometry, Ed. K. D. Mielenz, Academic Press, 195 (1982).

25. S. Buell and J. N. Demas, "A Simple Cell for Deoxygenation of Surfactant Containing Solutions", Rev. Sci. Instrum., in press.

26. C. M. Flynn, Jr. and J. N. Demas, "A Simple High Yield Preparation of Tris(oxaloto)iridate(III) with a Novel Solvent Extraction Step", Inorg. Chim. Acta (Lett.), in press.

27. T. D. L. Pearson and J. N. Demas, "An Axes Drawing Program for the 9872A and 7225A Digital Plotters," J. Chem. Ed., accepted.

28. T. D. L. Pearson, J. N. Demas, and S. Davis, "An Autozeroing Microcomputerized Boxcar Integrator", Anal. Chem., accepted.

29. K. Mandal, T. D. L. Pearson, W. P. Krug, and J. N. Demas, "Singlet Energy Transfer from the Charge Transfer Excited State of Tris(2,2'-bipyridine) ruthenium (II) to Laser Dyes", J. Am. Chem. Soc., accepted.

30. S. Buell and J. N. Demas, "Heterogenous Preparation of Singlet Oxygen Using an Ion-Exchange Bound Tris(2,2'-bipyridine) ruthenium(II) Photosensitizer", submitted.

31. K. Mandal, B. L. Hauenstein, Jr., J. N. Demas and B. A. DeGraff, "Interactions of Ruthenium(II) Photosensitizers with Triton X-100 Surfactant", submitted.

32. B. L. Hauenstein, Jr., K. Mandal, J. N. Demas, and B. A. DeGraff, "Electron Transfer Quenching of Ruthenium(II) Photosensitizers by Mercury(II) Chlorides. I. Reactions in Aqueous Solution.", submitted.

33. W. J. Dressick, B. L. Hauenstein, Jr., J. N. Demas, and B. A. DeGraff, "Electron Transfer Quenching of Ruthenium(II) Photosensitizers by Mercury(II) Chlorides. II. Reactions in Aqueous Sodium Lauryl Sulfate Micellar Solutions.", submitted.

34. J. C. Love and J. N. Demas, "Excited State Lifetime Measurements: Linearization of the Förster Equation by the Phase Plane Method", submitted.

E. Professional Personnel Involved in Work.

Postdoctorals:

S. H. Peterson
W. P. Krug
W. Dressick
K. Mandal
B. Hauenstein

Graduate Students:

D. G. Taylor
S. Buell
B. Carraway
T. J. Turley
T. D. L. Pearson
S. Snyder

Undergraduates:

M. Greer
E. Cetron
J. Toney
F. W. Reed
J. Love
J. Cline, Jr.

F. Interactions

1. J. N. Demas, "New Laser Dye Systems" at "Meeting on Laser Dye Lifetime Studies". Wright-Patterson Air Force Base. September 7, 1978. A meeting of Air Force and Navy researchers in laser dyes sponsored by the AFOSR.

2. J. N. Demas, "Excited-State Electron-Transfer Reactions of Transition Metal Complexes", with B. A. DeGraff and D. G. Taylor. Savannah ACS, November 10, 1978. Invited talk in the section on Chemical Conversion and Storage of Solar Energy.

3. W. P. Krug and J. N. Demas, "Spectroscopy of -Diimine Complexes of Ruthenium(II)", National ACS Meeting, Washington, D. C.. September, 1979.

4. T. D. L. Pearson and J. N. Demas, "A High Accuracy Microcomputerized Quantum Counter Comparator", Regional American Chemical Society Meeting at Roanoke, VA. November 1979.

5. J. N. Demas, "Excited State Energy and Electron Transfer Processes of Ruthenium(II) Complexes", invited talk at the University of New Mexico. December, 1979.

6. J. N. Demas, "Excited State Processes in Platinum Metal Complexes", invited talk at Los Alamos Scientific Research Laboratory. December, 1979.

7. J. N. Demas, "Platinum Metals and Solar Energy Conversion", invited talk to the American Chemical Society Student Chapter at the University of Virginia. March, 1980.

8. T. J. Turley and J. N. Demas, "A Microcomputerized Ultrahigh Speed Transient Record", Pittsburg Analytical Spectroscopy Meeting at Atlantic City. March, 1980.

9. T. D. L. Pearson, E. Cetron, and J. N. Demas, "A Microcomputerized Quantum Counter Comparator", Pittsburg Analytical Spectroscopy Meeting at Atlantic City. March, 1980.

10. F. Reed and J. N. Demas, "An Analysis of Errors in the Phase-Plane Method of Deconvoluting Luminescence Lifetimes", invited paper at the NATO Advanced Study Institute in Saint Andrews, Scotland. March, 1980.

11. J. N. Demas, "Excited State Energy and Electron

Transfer Processes of Platinum Metal Complexes", invited talk at IBM Watson Research Lab., N. Y. April, 1980.

12. D. G. Taylor and J. N. Demas, "A Microcomputerized Instrument for Studying Reversible Excited- State Electron-Transfer Reactions by the Step Excitation Method". SE/SW Regional ACS meeting, New Orleans, Louisiana, December, 1980.

13. D. G. Taylor and J. N. Demas, "Excited State Electron Transfer Reactions Studied by the Step Excitation Method", VIII IUPAC Symposium on Photochemistry, Seefeld, Austria, July 1980.

14. T. D. L. Pearson, E. Cetron and J. N. Demas, "A Versatile Microcomputerized Quantum Counter Comparator", VIII IUPAC Symposium on Photochemistry, Seefeld, Austria, July 1980.

15. K. Mandal, T. D. L. Pearson and J. N. Demas, "New Luminescent Quantum Counter Systems", VIII IUPAC Symposium on Photochemistry, Seefeld, Austria, July 1980.

16. D. G. Taylor and J. N. Demas, "Reversible Excited State Electron Transfer Reactions of Transition Metal Complexes", SERI Conference, August, 1980.

17. K. Mandal, T. D. L. Pearson and J. N. Demas, "Polymer Based Luminescent Quantum Counters", SERI Conference, August, 1980.

18. T. D. L. Pearson, E. Cetron and J. N. Demas, "Micro-computerized Quantum Counter Comparator", SERI Conference, August, 1980.

19-23. J. N. Demas, "Excited State Energy and Electron Transfer Processes of Metal Complexes", invited talk at Rutgers, New Jersey, March 12, 1981.

20. Invited talk at University of Pittsburgh, Penn., April 9, 1981.

21. Invited talk at Seton Hall, New Jersey, March, 10 1981.

22. Invited talk at Stevens Institute of Technology, March 11, 1981.

23. J. N. Demas, invited talk at Kean College, New Jersey, March 12, 1981.

24. T. D. L. Pearson, S. A. Davis, and J. N. Demas, "An Autozeroing Microcomputerized Boxcar Integrator with Subnanosecond Risetime", 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

25. D. G. Taylor and J. N. Demas, "A Microcomputerized Instrument for Studying Reversible Excited-State Electron-Transfer Reactions by the Step Excitation Method", 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

26. J. N. Demas, B. Hauenstein, and K. Mandal, "Excited State Energy and Electron Transfer Processes of Ruthenium(II) Photosensitizers", Invited talk at the ACS Awards Symposium in Inorganic Chemistry at the ACS Meeting in Las Vegas, April 1982.

27. J. N. Demas, "Luminescent Complexes, Micelles, and Togetherness", University of Richmond, April, 1982.

28. J. N. Demas, "Luminescent Complexes, Micelles, and Togetherness", New Mexico State University, April, 1982.

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